

NMR relaxation study of molecular motions between unequal potential wells in solid *trans,trans*-muconodinitrile^{a)}

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We report observations of extremely unusual proton NMR relaxation rates in solid *trans,trans*-muconodinitrile (TMD, $\text{N}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{C}\equiv\text{N}$). In particular we measured, over the temperature range 77–423 °K, proton dipolar relaxation times T_{1D} and spin lattice relaxation times T_1 (at 24 and 58 MHz). The relaxation pattern is characterized by the following features: (a) very long motional T_1 and T_{1D} even at their respective minima, (b) no detectable motional narrowing of the line even at the T_{1D} minimum, (c) unequal slopes at temperatures below and above the minimum of T_1 (and T_{1D}) vs $1/T$, and (d) significant deviations from the usual linear dependence on resonance frequency of the values of the relaxation times at their respective minima. We extended an earlier NMR theory to the case of spin lattice relaxation due to molecular reorientations between the extremely unequal potential energy wells of TMD. We were able to explain all features of the above data in terms of this theory. By comparing our data to the results of several calculations of intermolecular potential energy which used different interatomic force parameters, we were able to rule out some of these, thereby determining the best choice for the parameters in this crystal. The detailed structure of this potential profile (i.e., relative depths of the wells and energy barriers hindering rotation) was then determined from the T_1 and T_{1D} data. We thus have observed and characterized in TMD a low concentration of orientational defects which occur when a molecule occupies a higher energy well. Our observations are probably the first of such extreme NMR relaxation effects due to motions between significantly inequivalent sites.

I. INTRODUCTION

The study of nuclear magnetic resonance (NMR) relaxation times has proven to be one of the most powerful tools for investigation of atomic motions. In particular, temperature and resonance frequency dependences of the spin lattice relaxation times of nuclei in solids can provide detailed information concerning characteristic times of nuclear motions and associated activation energies.

Molecular crystals studied by NMR relaxation times typically have ordered structures and, for the case of molecular reorientations, the axis of hindered rotation usually coincides with a symmetry axis so that motion occurs between crystallographically (and therefore energetically) equivalent sites. Common examples are methyl's rotation about its C_3 axis and benzene's rotation about its C_6 axis. The detailed NMR relaxation theories for such cases are well established both in the high field "weak-collision" region,¹ where the internuclear dipolar interaction is treated as a motionally modulated perturbation, and in the low field "strong-collision" region,² in which the relaxation times are sensitive to much slower motions. Normally, a symmetric minimum in a plot of the temperature dependence of the spin lattice relaxation time is observed when the characteristic frequency of motion is comparable to the resonance frequency. Furthermore, high field spin lattice relaxation times (T_1) for proton resonance at the minimum are typically of the order of 1–100 msec, depending on the internuclear distances and

the orientation of the internuclear vectors relative to the axis of motion. Shorter times are obtained for rotating frame relaxation ($T_{1\rho}$) and even shorter for dipolar relaxation (T_{1D}). The T_{1D} minimum usually occurs at temperatures corresponding to the onset of motional narrowing. Furthermore, fluctuations of the *entire* dipolar Hamiltonian occurring at a frequency of order $1/T_2$ cause the value of T_{1D} at the minimum to be comparable to T_2 .

These features are also typical of molecular reorientations in plastic crystals, even though jumps may then occur between crystallographically inequivalent sites. Nevertheless, as long as motions occur in the orientationally disordered crystals between energetically equal or very similar potential wells, one may expect the above mentioned general behavior to characterize the relaxation.

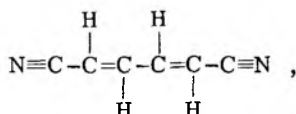
A third class of crystals is characterized by what can be called orientational defects. For these crystals a fraction of the molecules can occupy metastable orientations corresponding to energies which are higher than that of the main minimum corresponding to the equilibrium orientation. When the energy difference between inequivalent orientations is high compared to the thermal energy of the molecules, the population in a sub-minimum is relatively small and therefore undetectable by diffraction techniques. NMR, on the other hand, measures relaxation rates which are sensitive to the dynamics of the nuclei and, accordingly, may detect molecular jumps between such unequal potential wells. In a preliminary paper³ we noted that such motions may lead to anomalous relaxation rates which differ from those observed in the more "normal" cases of motions between equivalent wells. As predicted theoretically,^{4,5} NMR relaxation in unequal wells is relatively inefficient. This inefficiency arises from incomplete di-

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polar averaging resulting from the relatively short time the molecules spend in a subminimum compared to their longer stay at the low-energy orientation. Only few NMR relaxation studies known to us⁶⁻⁹ have been devoted to crystals of this type. Moreover, in the majority of these studies the energy difference between wells was typically of the order of the average thermal energy. In this case the relaxation rates show nearly normal behavior. At the other extreme, where the well difference is far greater than kT , the population of the subminima may be too small for this mechanism to dominate the relaxation.

The study reported here deals with *trans,trans*-muconodinitrile (TMD)



which, according to our results, is intermediate between the above two cases. Specifically, in this crystal reorientations can occur between unequal potential wells whose differences in energy at the respective minima are considerably larger than kT but still not too big to provide a completely inefficient NMR relaxation mechanism. Thus, the relaxation effects observed for the protons of TMD show that at room temperature about half a percent of the molecules occupy metastable orientations. The observed behavior exhibits the following unique features:

(1) We observed extremely long spin lattice relaxation times (T_1 , $T_{1\rho}$, T_{1D}) approximately three orders of magnitude longer than in the usual equal wells case.

(2) No motional narrowing was observed in T_2 measurements even at temperatures above the T_{1D} minimum. Moreover, the value of T_{1D} at the minimum is about four orders of magnitude larger than the corresponding T_2 . This behavior is in contrast to the situation characterized by fluctuations of the entire dipolar energy resulting in T_{1D} at the minimum being of order T_2 .

(3) We observed considerably different slopes above and below the T_1 minimum in the T_1 vs reciprocal temperature plot.

(4) The frequency dependence of the relaxation time minima is weaker than the usual linear relationship.

In Sec. V we analyze these peculiar data on the basis of a model of molecular jumps between unequal wells using an NMR relaxation theory developed for slightly different cases by Look and Lowe⁴ and by Anderson.⁵ Since their treatments are confined to equal barriers, we extended their equations to somewhat more general potential energy surfaces, such as those which occur for TMD's molecular rotations in the crystal.

An independent calculation¹⁰ of the potential energy for reorientations of TMD using a van der Waals atom-atom potential function indicates that, when a TMD molecule reorients about its long axis, there exist in the crystal two subminima between three energy barriers of different heights. These theoretical results

are only qualitative, primarily because the different van der Waals parameters introduced in the literature give somewhat different well depths and energy barriers. The analysis of the NMR relaxation data (Sec. V) provides a detailed quantitative description of the energy surface for molecular reorientations in solid TMD and thus allows one to determine the best set of van der Waals parameters for this case.

II. THEORY

A. NMR relaxation due to motions between unequal wells

Motions between unequal wells constitute a distinct and unique NMR relaxation mechanism because such motions may bring about a partial and correspondingly smaller averaging of the local dipolar fields than do motions between symmetric minima. The limited fluctuation in local fields is directly related to the relative populations at the potential minima and is therefore temperature dependent. Thus, in addition to the usual effects of temperature on the correlation times characterizing the motions, temperature further affects the relaxation through its gradual effect on the degree of dipolar averaging.

Theoretical studies of the problem were done by Look and Lowe⁴ for the case of motions in two unequal potential wells and by Anderson⁵ for a three well potential. In particular, Anderson examined effects of reorientations for a potential in which two of the minima have equal depth higher in energy than the equilibrium minimum (Fig. 1).

For thermally activated motions the jump probabilities are given by

$$k_1 = K \exp[-(H + \Delta)/RT] \quad (1)$$

and

$$k_2 = K \exp(-H/RT).$$

As we discuss in Sec. IV, the energy surface in an actual crystal may differ considerably from this relatively symmetric case. TMD exhibits a much more asymmetric potential and this was taken into account when using the expressions derived. Nevertheless, the basic assumptions and approach are still the same, namely, that the reorientation process consists entirely of individual jumps to adjacent sites. Also, we assume that the energy barriers are the same for all molecules and further assume that there is no correlation between motions of different molecules.

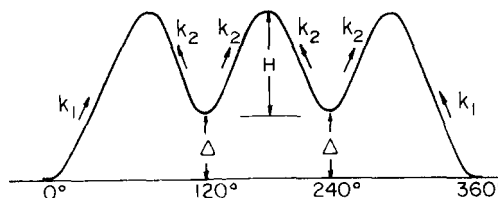


FIG. 1. Three well potential energy profile for molecular reorientation. In this model the jump probability k_2 is greater than k_1 .

Even though we are studying a dipolar minimum the low temperature side of which would normally be analyzed by a strong collision theory,² we used a weak collision perturbation approach in evaluating the relaxation rates for the entire relaxation curves. This approach seems to be justified, since a molecule which jumps from a low energy minimum to a subminimum at a rate, say, $\tau^{-1} \sim T_2^{-1}$, will jump out of the subminimum in a much shorter time and thus cannot be described by a spin temperature prior to this second jump. In a later section of this paper we present experimental results which demonstrate the inapplicability of the strong collision theory.

The dipolar and spin lattice relaxation effects due to the small fraction of the dipolar interactions which is modulated by the motion can be treated by the usual perturbation theory. The correlation function for the modulation of the dipole-dipole interactions is evaluated by solving the differential equations characterizing the dynamics of nuclei in the potential surface. Their solution gives the time dependence of the probabilities of finding a molecule at each orientational site. According to Anderson, the correlation function for the case of three equally spaced orientations (Fig. 1) consists of a linear combination of two exponentials with decays characterized by different correlation times. After powder averaging, the high field and the dipolar relaxation rates are given, respectively, by

$$T_1^{-1} = \frac{\gamma^2 (M_2)_{\text{mod}}}{2} \left[3Q_1 Q_2 \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{4\tau_1}{1 + 4\omega_0^2 \tau_1^2} \right) + Q_2 \left(\frac{\tau_2}{1 + 4\omega_0^2 \tau_2^2} + \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2} \right) \right] \quad (2a)$$

and

$$T_{1D}^{-1} = \frac{3\gamma^2 (M_2)_{\text{mod}}}{2} \left[3Q_1 Q_2 \left(\frac{\tau_1}{1 + 4\omega_D^2 \tau_1^2} \right) + Q_2 \left(\frac{\tau_2}{1 + 4\omega_D^2 \tau_2^2} \right) \right] \quad (2b)$$

In Eqs. (2) Q_1 and Q_2 are the steady-state probabilities of finding a molecule at the equilibrium and metastable orientations, respectively, and are given in terms of the jump probabilities k_1 and k_2 by

$$Q_1 = \frac{k_2}{k_2 + 2k_1}, \quad Q_2 = \frac{k_1}{k_2 + 2k_1} \quad (3)$$

The correlation times τ_1 and τ_2 are given in terms of the same jump probabilities $\tau_1^{-1} = k_2 + 2k_1$ and $\tau_2^{-1} = 3k_2$. $(M_2)_{\text{mod}}$ is the total motional change in the second moment when the wells are equal (i. e., $\Delta = 0$), ω_0 is the high field Larmor frequency, and ω_D is the precession frequency in the local field H_D and is given by $\omega_D = \gamma \langle H_D^2 \rangle^{1/2}$. [If the three well depths are equal, $k_1 = k_2 = \frac{1}{3} \tau_1^{-1} = \frac{1}{3} \tau_2^{-1}$ and $Q_1 = Q_2 = 1/3$, so Eqs. (2a) and (2b) reduce to the usual spin lattice relaxation rate expressions.]

In case the energy barriers or the subminima depths are not equal, Eqs. (2a) and (2b) must be modified somewhat, as we shall see in Sec. V. Nevertheless, the same general features characterize the expected relaxation behavior: (1) Spin lattice and dipolar relaxation times are longer than in the usual case of motions

between equal potential wells; furthermore, larger energy differences Δ between wells will result in longer relaxation times. (2) Motional narrowing is inhibited and, if the energy difference between the wells is far greater than kT , may be too small to be observed. As explained before, the origin of these phenomena is the decrease in rms fluctuations of the local fields with increasing well difference Δ , since a larger energy difference causes a larger proportion of the molecules to occupy the low energy equilibrium position.

B. Application to motions between extremely unequal wells ($\Delta \gg RT$)

Our potential energy calculations¹⁰ for TMD indicate that, at all temperatures up to the melting point, the condition $\Delta \gg RT$ is satisfied. As we shall now show, this feature results in rather dramatic effects on the relaxation.

In the limit $\Delta \gg RT$, k_2 is much larger than k_1 with the result that

$$Q_1 \cong 1, \quad Q_2 \cong \frac{k_1}{k_2} = \exp(-\Delta/RT). \quad (4)$$

Then Eqs. (2) reduce to

$$T_1^{-1} = \frac{\gamma^2 (M_2)_{\text{mod}}}{2} \exp(-\Delta/RT) \left[3 \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{4\tau_1}{1 + 4\omega_0^2 \tau_1^2} \right) + \left(\frac{\tau_2}{1 + \omega_0^2 \tau_2^2} + \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2} \right) \right] \quad (5a)$$

and

$$T_{1D}^{-1} = \frac{3\gamma^2 (M_2)_{\text{mod}}}{2} \exp(-\Delta/RT) \left(\frac{3\tau_1}{1 + 4\omega_D^2 \tau_1^2} + \frac{\tau_2}{1 + 4\omega_D^2 \tau_2^2} \right) \quad (5b)$$

Furthermore, when $\Delta \gg RT$, $\tau_1 = 3\tau_2 = \tau_0 \exp(H/RT)$.

We can see several striking results of these equations:

(1) Relaxation times become longer by the inverse Boltzmann factor $\exp(\Delta/RT)$ compared to those for motions between equal wells.

(2) The slopes of a plot of the temperature dependence of each relaxation time are different above and below the minima. At temperatures above the minimum $\omega\tau \ll 1$ and

$$T_1, T_{1D} \propto \exp[(\Delta - H)/RT], \quad (6a)$$

whereas at temperatures below the minimum $\omega\tau \gg 1$ and

$$T_1, T_{1D} \propto \exp[(\Delta + H)/RT]. \quad (6b)$$

Thus, a measurement of the high and low temperature slopes of the relaxation time vs temperature enables one to determine Δ and H separately.

(3) The factor $\exp(-\Delta/RT)$ shifts the position of the minima. In Fig. 2 we calculated the value of $(\omega\tau)_{\text{min}}$ as a function of Δ/H for both the T_1 and T_{1D} minima. The mathematical form of $(\omega_0\tau)_{\text{min}}$ vs Δ/H for a T_1 minimum is rather complicated and was calculated numerically. On the other hand, for a T_{1D} minimum, $(\omega_D\tau)_{\text{min}}$ is given by

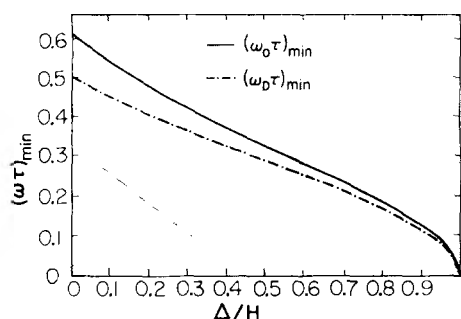


FIG. 2. Theoretical position of the relaxation minima vs Δ/H . The position is characterized here by $(\omega_0\tau)_{\min}$ [or $(\omega_D\tau)_{\min}$] for T_1 (or T_{1D}).

$$(\omega_D\tau)_{\min} = \frac{1}{2} \sqrt{\frac{H-\Delta}{H+\Delta}} \quad (7)$$

As we can see for both cases, the effect on unequal wells is to shift the relaxation time minima towards higher temperatures compared to their position when $\Delta = 0$.

(4) A final interesting feature is that the factor $\exp(-\Delta/RT)$, which causes an upward shift in the magnitude of all relaxation times, results in reduced frequency dependence of the value of T_1 (or T_{1D}) at their minima. Since $1/T_1 \propto [\exp(-\Delta/RT)]/\omega_0$ and $1/T_{1D} \propto [\exp(-\Delta/RT)]/\omega_D$ at their respective minima, it is easy to see that for any relaxation time at its minimum, we have that

$$(T_1)_{\min} \propto (\omega_0)^{1-(\Delta/H)} \quad (8a)$$

and

$$(T_{1D})_{\min} \propto (\omega_D)^{1-(\Delta/H)} \quad (8b)$$

For unequal wells we thus have a reduced frequency dependence of the value of T_1 (or T_{1D}) at the minimum compared to the linear frequency dependence which holds for motions between equal wells ($\Delta/H = 0$). This can result in a much shallower minimum for T_{1D} than is usually the case (see Fig. 3).

In Sec. IV of this paper we shall report experimental

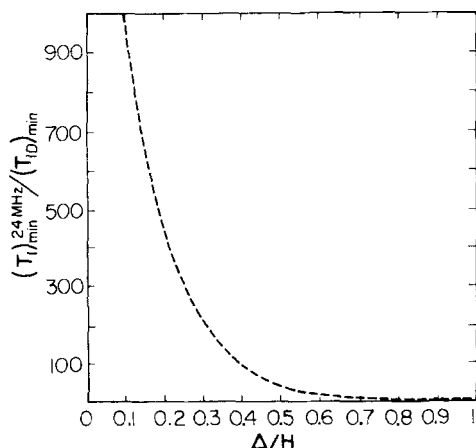
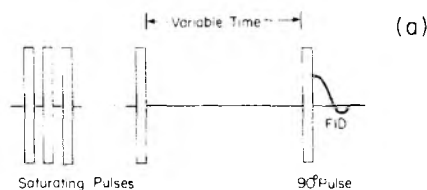


FIG. 3. Theoretical ratio of relaxation times at the minima $(T_1)_{\min}(24 \text{ MHz})/(T_{1D})_{\min}$ vs Δ/H . Note that, in the limit $\Delta \rightarrow H$, $(T_{1D})_{\min}$ approaches $(T_1)_{\min}$ and thus the dependence on rf frequency disappears.

PULSE SEQUENCE FOR T_1 MEASUREMENT



PULSE SEQUENCE FOR $T_{1\rho}$ (or T_{1D}) MEASUREMENT

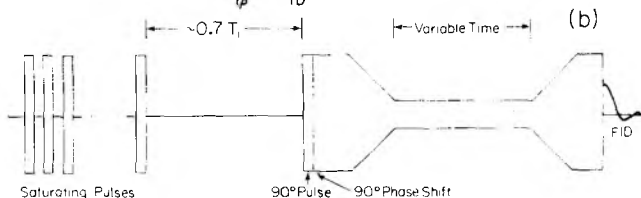


FIG. 4. Pulse sequences used in measuring relaxation times.

observations on TMD which exhibit each of these interesting predictions.

III. EXPERIMENTAL PROCEDURE

A. NMR pulse sequence

The spin lattice relaxation times were measured at rf frequencies of 24 and 58 MHz by applying a train of a few close-spaced 90° saturating pulses followed at a variable time interval by a single probing 90° pulse [Fig. 4(a)]. The train of closely spaced pulses destroys all residual magnetization in a relatively short time, thereby eliminating the need for waiting several T_1 's between measurements as in the conventional $180^\circ-90^\circ$ or $90^\circ-90^\circ$ sequences. This technique is particularly advantageous when T_1 is long, as in the case of TMD for which the protons' T_1 at 24 MHz is 40 min at 77°K !

The same method of preparative saturation was used in measuring the dipolar relaxation time T_{1D} and the rotating frame spin lattice relaxation time $T_{1\rho}$ in order to avoid a long delay between cycles. The $T_{1\rho}$ (or T_{1D}) measurements were then made by waiting a constant time of about $0.7T_1$ after the saturating pulse train and then applying a "spin-lock" sequence (90° pulse- 90° phase shift) followed by adiabatic demagnetization (ADRF) to a low (or zero) H_1 value. After waiting a variable time, $T_{1\rho}$ (or T_{1D}) is measured by adiabatic remagnetization along H_1 and then observation of the magnitude of the initial signal following a sharp turnoff of H_1 as a function of time in the demagnetized state (see Fig. 4(b)).

In some preliminary T_{1D} measurements we used adiabatic frequency modulation¹¹ instead of the spin-lock method in order to tilt the magnetization into the H_1 direction. This frequency modulation was followed as before by ADRF of H_1 to zero field and subsequent remagnetization. Exact resonance is critically important in measuring T_{1D} and is achieved by adjusting H_0 to give no signal for zero-field times much greater than T_{1D} .

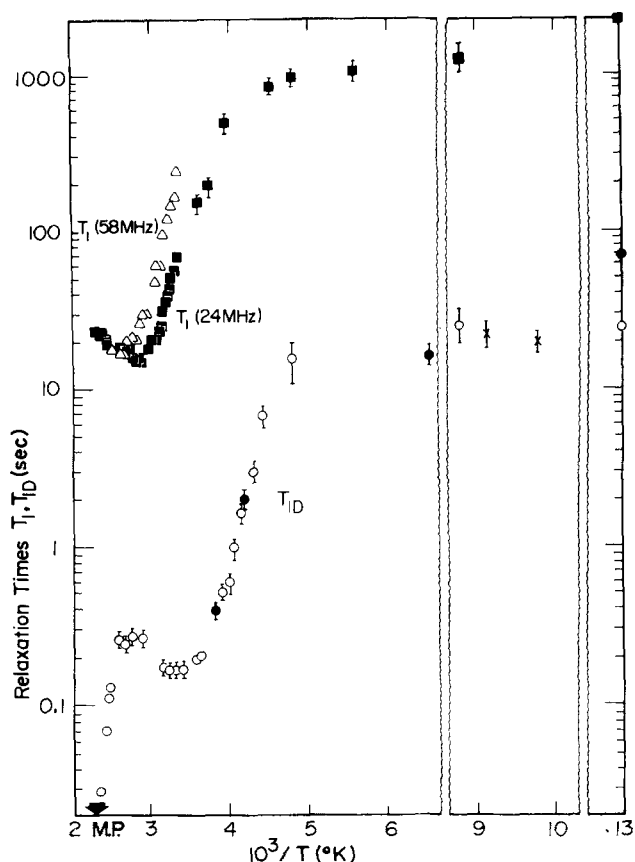


FIG. 5. Measured relaxation times vs inverse temperature in polycrystalline TMD. Open and black circles refer to T_{1D} of sample I before and after exposure to elevated ($\sim 150^\circ\text{C}$) temperatures, respectively. The crosses are T_{1D} values for sample II, which was not exposed to elevated temperatures. Squares and triangles refer to T_1 of sample I at 24 and 58 MHz, respectively.

B. Characteristics of TMD sample

The powder sample used in the experiments described in this paper was prepared at the University of Tel-Aviv by a procedure described in detail elsewhere.¹² The muconodinitrile was synthesized in a two step gas-solid reaction. The *trans,trans* isomer was then separated from the other isomers by recrystallization from ethanol and identified by its melting point (159°C).

The extremely long T_1 values which we observed at low temperatures indicate that the sample had a relatively low impurity content. Upon excessive heating the white powder turns gradually darker, probably due to polymerization.

IV. EXPERIMENTAL RESULTS

In order to obtain information about the detailed shape of the potential energy surface, we measured proton spin lattice relaxation times of polycrystalline TMD over wide ranges of resonance frequencies and temperatures. The temperature dependence of T_{1D} and of T_1 at 24 and 58 MHz are plotted in Fig. 5 and exhibit a number of interesting features, which we summarize below. In the

next section of this paper we will discuss the results in terms of the theory presented in Sec. II.

(1) The observed relaxation rates are extremely low even at the T_1 and T_{1D} minima. Thus, the minimal T_{1D} value is 0.16 ± 0.01 sec, compared to more typical values of 0.1–1 msec.

(2) Within the accuracy of the FID measurements T_2 appears to be temperature independent ($13 \pm 2 \mu\text{sec}$). Thus, using this technique, we didn't observe any detectable motional narrowing even at temperatures corresponding to the T_{1D} minimum, which is extremely long compared to T_2 . The second moment of the absorption line at the temperature of the T_{1D} minimum (approximately room temperature) was measured earlier by cw and pulse techniques.^{12,13} Only a very small reduction ($\sim 8\%$) from the calculated rigid-lattice value was observed. It was attributed to librational effects.

(3) The slope of T_1 vs $1/T$ above the minimum is considerably smaller than the slope at temperatures below the minimum, as can be seen in Fig. 6. The same effect may possibly be seen when comparing the slope of T_{1D} vs $1/T$ below its minimum to the slope right above the minimum; however, it is difficult to estimate an accurate value for this high temperature slope since another mechanism, which becomes dominant at about 385°K , causes T_{1D} to drop sharply with temperature. At temperatures below $\sim 200^\circ\text{K}$ there is a considerable decrease in the slopes of both T_1 and T_{1D} , which indicates that a different mechanism dominates the spin lattice relaxation over the range from this temperature down to the lowest temperature measured in this study (liquid N_2). Therefore, in order to eliminate the contributions of this mechanism to the higher tem-

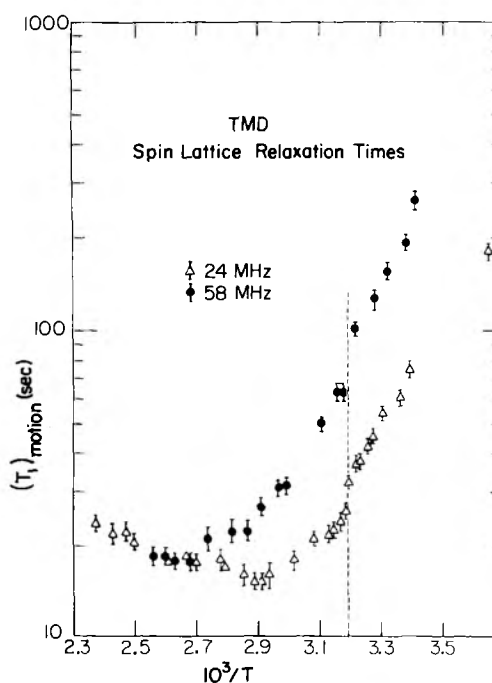


FIG. 6. Motional contribution to T_1 vs inverse temperature (expanded scale). The discontinuity in the T_1 's at $10^3/T = 3.19^\circ\text{K}^{-1}$ is indicated by the vertical dashed lines. Note the differences in slope below and above the minima.

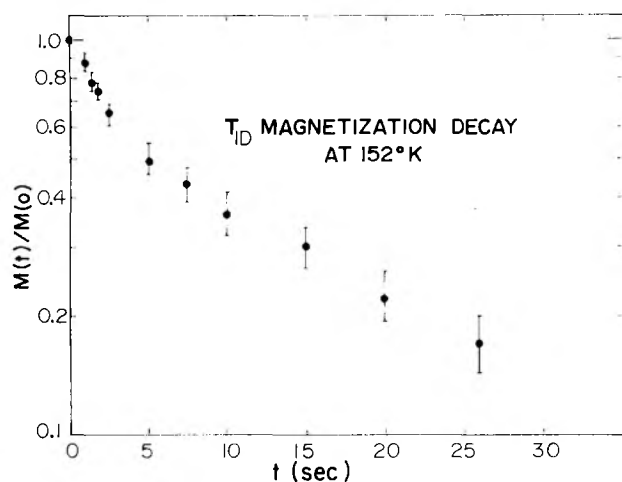


FIG. 7. Magnetization in TMD vs time in the demagnetized state following the spin-lock ADRF pulse sequence of Fig. 4(b).

perature relaxation, we had to subtract from the observed rates the extrapolated relaxation rates due to that mechanism

$$\left(\frac{1}{T_{1,D}}\right)_{\text{motion}} = \frac{1}{T_{1,D}} - \left(\frac{1}{T_{1,D}}\right)_{\text{extrap}} \quad (9)$$

Thus, for data analysis we used relaxation times $(T_{1,D})_{\text{motion}}$ obtained from Eq. (9) rather than the observed values. [In Fig. 5 we plotted observed values, whereas in Fig. 6 we used $(T_1)_{\text{motion}}$ values corrected according to Eq. (9).] The slopes were evaluated by assuming thermally activated processes (Table I). Because of the differences in slopes between T_1 and $T_{1,D}$, it appears that they probably reflect different mechanisms. Furthermore, the T_1 and $T_{1,D}$ minima occur at surprisingly close temperatures for them to reflect the same mechanism, specifically, 305 °K vs 345 °K for $(T_{1,D})_{\text{min}}$ and $(T_1)_{\text{min}}$ (24 MHz), respectively.

(4) The frequency dependence of the spin lattice relaxation times at the respective minima is smaller than that usually observed

$$\frac{(T_1)_{\text{min}}(58 \text{ MHz})}{(T_1)_{\text{min}}(24 \text{ MHz})} = 1.13 \pm 0.07, \quad \frac{(T_{1,D})_{\text{min}}(24 \text{ MHz})}{(T_{1,D})_{\text{min}}} = 94 \pm 9.$$

(5) The $T_{1,D}$ values measured at the lowest temperature range (below 200 °K) seem to depend on the sample used and whether it was previously exposed to elevated temperatures ($\sim 150^\circ\text{C}$). Moreover, unlike the results at higher temperatures, the magnetization in this region didn't go to zero exponentially as the demagnetization time was increased in the $T_{1,D}$ measurement (see Fig. 7).

(6) A break in the slope of T_1 appears at around 40 °C ($10^3/T$ equals 3.19°K^{-1}) in both the 24 and 58 MHz data. In Fig. 6 T_1 values corrected for the low-temperature mechanism are plotted with an expanded $1/T$ scale in order to display the observed small ($\sim 20\%$) discontinuity. In the next section we will present possible explanations for this effect and the one mentioned

TABLE I. Experimental values^a of $H - \Delta$ and $H + \Delta$.

Relaxation time	$H - \Delta$ (kcal/mole) (temperatures above minimum)	$H + \Delta$ (kcal/mole) (temperatures below minimum)
T_1	1.6 ± 0.2	7.7 ± 0.5
$T_{1,D}$	3 ± 1	11 ± 1

^aThese were obtained for TMD from experimental slopes at temperatures above and below the minima of $\log T_1$ (or $T_{1,D}$) vs $1/T$.

in (5), neither of which are related to the main relaxation mechanism.

In order to investigate further the mechanism responsible for the $T_{1,D}$ minimum, we measured the rotating frame spin lattice relaxation time $T_{1\rho}$ for different values of the rf field H_1 at two different temperatures, below and at the $T_{1,D}$ minimum. According to the strong collision theory², $T_{1\rho}$ should have the following dependence on H_1^2 :

$$T_{1\rho} \propto \frac{H_1^2 + H_D^2}{H_D^2} \quad (10)$$

Normally, this theory would apply only to the region below the $T_{1\rho}$ minimum. As can be seen in Fig. 8, $T_{1\rho}$ follows the H_1^2 law at both temperatures. However, for the temperature below the $T_{1,D}$ minimum (250 °K) we see that the horizontal intercept occurs at a field significantly higher than the local field H_D . The square of the local field was estimated to be $1/3$ of the experimental second moment of the TMD protons' absorption line¹² ($3.3 \pm 0.1 \text{ g}^2$) despite the fact that this value was measured at 300 °K. We felt justified in neglecting changes due to temperature in the effects of librations on the second moment,¹³ since they do not depend strongly on temperature. Accordingly, we used at 250 °K the value 1.1 g^2 for H_D^2 .

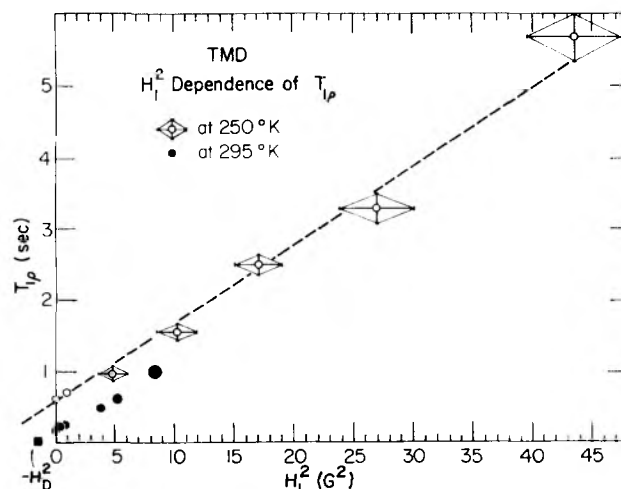


FIG. 8. Rotating-frame relaxation time $T_{1\rho}$ vs H_1^2 (square of rf field amplitude). H_D^2 is the square of the dipolar local field measured in Ref. 12. The data at 250° (open circles) do not have a horizontal intercept at $-H_D^2$, thereby indicating the inapplicability of the strong collision theory.

V. DISCUSSION

A. NMR determination of TMD well differences and energy barriers

The anomalous NMR relaxation pattern observed for TMD's protons above $\sim 200^\circ\text{K}$ is indicative of nuclear motion between unequal potential wells as discussed in Sec. II. This experimental evidence is consistent with results calculated for the potential energy surface which in turn suggest the existence of such wells when a TMD molecule is reorienting around its long axis.¹⁰ As predicted earlier by Look and Lowe⁴ and by Anderson,⁵ such a relaxation mechanism is less efficient than motions between equal wells because in the unequal case a smaller fraction of the dipolar local field is modulated by the motions. This leads to longer spin lattice relaxation times and to inhibition of the apparent motional narrowing. A rough estimate of the fraction of the dipolar interaction which is averaged out by TMD's molecular motions can be obtained from the experimental ratio $(T_{1D})_{\min}/(T_2)_{\text{RL}}$. According to Eq. (2b) T_{1D}^{-1} at the minimum is given by

$$(T_{1D})_{\min}^{-1} \propto \frac{(M'_2)_{\text{mod}}}{\omega_D} \propto \frac{(H_D^2)_{\text{mod}}}{(H_D)_{\text{RL}}}, \quad (11)$$

where $(H_D)_{\text{RL}}$ and $(H_D^2)_{\text{mod}}$ are, respectively, the rigid-lattice dipolar local field and the change in the square of the local field due to motions. [Note that $(M'_2)_{\text{mod}}$ is appropriate to wells which may be unequal and would then be smaller than the $(M_2)_{\text{mod}}$ defined earlier. For $\Delta \gg RT$, $(M'_2)_{\text{mod}} \cong (M_2)_{\text{mod}} \exp(-\Delta/RT)$.] Since $(T_2)_{\text{RL}}^{-1} \propto (H_D)_{\text{RL}}$, we have that

$$\frac{(T_{1D})_{\min}}{(T_2)_{\text{RL}}} \approx \frac{(H_D^2)_{\text{RL}}}{(H_D^2)_{\text{mod}}}. \quad (12)$$

For the usual situation in which there is appreciable motional narrowing $(H_D^2)_{\text{mod}} \sim (H_D^2)_{\text{RL}}$ and $(T_{1D})_{\min} \sim (T_2)_{\text{RL}}$. We observed for TMD a ratio of 1.3×10^4 , so only about 10^{-4} of the square of the local dipolar field (or second moment) is averaged out at room temperature by the motions! In contrast, we estimated a 30% reduction in the second moment of polycrystalline TMD in case the motions were between three *equal* wells along the same axis. The large difference between this result and our observations indicates the existence of a large energy difference between the main minimum and the higher subminima of the potential curve.

As discussed in the previous section, the data suggest that the T_1 and T_{1D} minima reflect different mechanisms. Furthermore, calculated potential energies¹⁰ suggest that the three energy barriers (and subminima depths) in TMD may be different in size. Accordingly, these differences should be taken into account when applying the relaxation equations to the present case. Fortunately, the spacing of the wells' minima in TMD occurs fairly close to 120° and 240° as in Anderson's theory. The general case of the three well potential was treated theoretically by Hoffman¹⁴ in his study of the expected effects of reorientations between unequal wells on dielectric relaxation. His general expressions for the time dependence of the wells' populations should, however, be transformed to fit the particular shape of

TMD's potential surface. The calculated energy profile indicates that the barrier corresponding to a relative orientation of 90° is considerably higher in energy than the other two barriers. Within the uncertainties of the calculation we are left with the possibilities that the central barrier is either higher (as in Fig. 9) or lower than the barrier at 260° . (The experimental evidence for the existence of two distinct relaxation mechanisms rules out the possibility of a two well potential in TMD, even though such a result could be obtained with one of the possible van der Waals parameter sets.¹⁵) Consistent with the evidence for large Δ_1 ($\Delta_1 \gg RT$) we assumed that the jump probability k_5 is significantly larger than k_6 (see Fig. 9). Since the barrier at 90° appears to be quite large, we further assumed that the jump probabilities k_1 and k_2 are considerably smaller than the rest. With regard to the relative heights of the barriers at 150° and 260° we found that only the potential surface consisting of a higher central barrier could fit the NMR data consistently. Figure 9 shows our model for the potential profile for reorientation of a single TMD molecule. Since the smallest barrier is at 260° , we found that it was reasonable to assume that $k_5 \gg k_3, k_4$. Using this model for the potential profile, we then predict the existence of two distinct correlation times for TMD and thus, in principle, the occurrence of two minima each in T_1 and in T_{1D} . In particular, the two relevant correlation times for these unequal wells turn out to be

$$\tau_1 \cong k_5^{-1} = \tau_0 \exp(H_1/RT) \quad (13a)$$

and

$$\tau_2 \cong k_3^{-1} = \tau_0' \exp(H_2/RT), \quad (13b)$$

where τ_2 is significantly longer than τ_1 . (It should be noted that we observed only one T_1 minimum and one T_{1D} minimum, for reasons to be discussed shortly.)

We then generalize Eqs. (5a) and (5b), respectively, to give for this case

$$T_1^{-1} = \frac{\gamma^2 (M_2)_{\text{mod}}}{2} \left[3 \exp(-\Delta_1/RT) \left(\frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{4\tau_1}{1 + 4\omega_0^2 \tau_1^2} \right) + \exp(-\Delta_2/RT) \left(\frac{\tau_2}{1 + \omega_0^2 \tau_2^2} + \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2} \right) \right] \quad (14a)$$

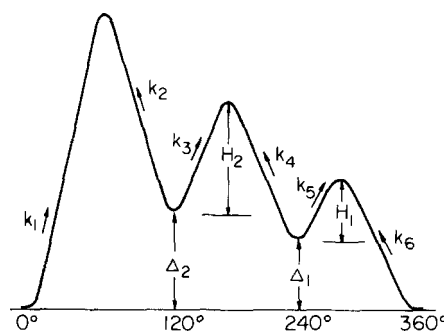


FIG. 9. Proposed three well model for potential energy vs orientation about its long axis of a single molecule in crystalline TMD. Jump probabilities between different wells obey the following relations: $k_1, k_2 \ll k_3, k_4, k_5, k_6$ and $k_5 \gg k_3, k_4, k_6$.

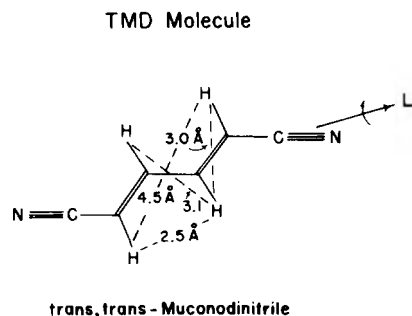


FIG. 10. Structure of a TMD molecule in the solid. Indicated are intramolecular interprotonic distances as well as the direction L of the inertia axis corresponding to the axis of molecular reorientation. The proton-proton distances were evaluated from the x-ray determined atomic positions of Filippakis *et al.*²⁴

and

$$T_{1D}^{-1} = \frac{3\gamma^2(M_2)_{\text{mod}}}{2} \left[\exp(-\Delta_1/RT) \left(\frac{3\tau_1}{1 + 4\omega_D^2\tau_1^2} \right) + \exp(-\Delta_2/RT) \left(\frac{\tau_2}{1 + 4\omega_D^2\tau_2^2} \right) \right], \quad (14b)$$

where τ_1 and τ_2 are given by Eqs. (13). Accordingly, the T_1 minimum seems to correspond to jumps over the low barrier H_1 , whereas the T_{1D} minimum would reflect motions over the higher central barrier H_2 . Hence, the four quantities of interest Δ_1 , H_1 and Δ_2 , H_2 can be evaluated from the T_1 and T_{1D} data, respectively. Equation (6a) would apply to T_1 relaxation at temperatures above the minimum $T_1 \propto \exp[(\Delta_1 - H_1)/RT]$, while for temperatures below the minimum Eq. (6b) gives $T_1 \propto \exp[(\Delta_1 + H_1)/RT]$. Similarly, the high and low temperature slopes of T_{1D} correspond to $(\Delta_2 - H_2)$ and $(\Delta_2 + H_2)$, respectively. So, both the energy difference Δ between the equilibrium and a metastable state and the activation energy H for a molecular jump from the metastable state are obtained individually from the sum and difference of slopes below and above the minimum. The results evaluated in this way (Table II) reveal that indeed $\Delta_1 \neq \Delta_2$ and $H_1 \neq H_2$.

As we have seen in Sec. II the wells' relative depths Δ_1 and Δ_2 can be evaluated also from the experimental

T_1 and T_{1D} minimum values, respectively. Using the graphs in Fig. 2 together with the experimental Δ/H ratios, we found that for both relaxation times in TMD a minimum should occur when $(\omega\tau)_{\text{min}} \approx 0.2$. In order to evaluate Δ from the value of the relaxation time at the minimum using Eqs. (14), it is also necessary to calculate the expected total change in second moment $(M_2)_{\text{mod}}$ due to motion around the same axis between *equal* wells. Using a well known formula,¹⁶ we calculated the change in the intramolecular contribution due to such motions to be only 0.65 g² (a 30% reduction). The smallness of the reduction is due mainly to the fact that the most significant internuclear vectors (i. e., the short vectors between the *cis* protons in Fig. 10) are almost parallel to the axis of motion and, accordingly, their orientations are not changed much by the motions. Assuming a similar reduction in the intermolecular contribution we get that $(M_2)_{\text{mod}}$ equals 1 g². The values of $(T_1)_{\text{min}}$ and $(T_{1D})_{\text{min}}$ obtained from experiment together with the above $(M_2)_{\text{mod}}$ and $(\omega\tau)_{\text{min}}$ give a value for Δ_1 of 3.2 ± 0.2 kcal/mole and for Δ_2 a value of 4.2 ± 0.2 kcal/mole, respectively, which agree very well with the results of the slopes' analysis (see Table II).

Another interesting aspect of the nuclear relaxation induced by motions between unequal potential wells which we predicted in Sec. II is the weaker dependence of the relaxation time minimum on the resonance frequency [Eq. (8)]. Again, the dominant factor is Δ/H and, for high field relaxation times such as at 24 and 58 MHz, the ratio of their respective minimum values should obey

$$\frac{(T_1)_{\text{min}}(58 \text{ MHz})}{(T_1)_{\text{min}}(24 \text{ MHz})} = \left(\frac{58}{24} \right)^{1-(\Delta/H)}. \quad (15)$$

As can be seen in Fig. 6 the experimental values for $(T_1)_{\text{min}}$ differ by only 13% (compared to an expected 240% if $\Delta = 0$)! This result leads to $\Delta/H = 0.86 \pm 0.07$, which is within the limits of the experimental error of the value obtained from the T_1 slopes' analysis (Table II). Such a ratio may explain the reason for our not having observed at lower temperatures a minimum in T_{1D} corresponding to the same mechanism as that responsible for the observed T_1 minimum. The calculated ratio $(T_1)_{\text{min}}/(T_{1D})_{\text{min}}$ is plotted as a function of Δ/H in Fig. 3. Note that $(T_{1D})_{\text{min}}$ becomes comparable to $(T_1)_{\text{min}}$ as Δ becomes

TABLE II. Orientational structure parameters^a of potential wells in TMD obtained from NMR measurements of relaxation times.

Method	Δ_1	H_1	Δ_2	H_2	Δ_1/H_1	Δ_2/H_2
$T_1(24 \text{ MHz})$ vs $1/T$ (slopes)	3.1 ± 0.3	4.6 ± 0.3			0.7 ± 0.1	
$(T_1)_{\text{min}}$ (24 MHz)	3.2 ± 0.2					
T_{1D} vs $1/T$ (slopes)			4 ± 1	7 ± 1		0.6 ± 0.2
$(T_{1D})_{\text{min}}$			4.2 ± 0.2			
$(T_{1D})_{\text{min}}/T_2$			5 ± 1			
$(T_1)_{\text{min}}(24 \text{ MHz})/(T_1)_{\text{min}}(58 \text{ MHz})$					0.86 ± 0.07	

^aIn particular, Δ_1 and Δ_2 refer to energy differences between the equilibrium and metastable states and H_1 and H_2 correspond to barrier heights measured from these metastable states (see Figs. 9 and 11). All energies are in kcal/mole.

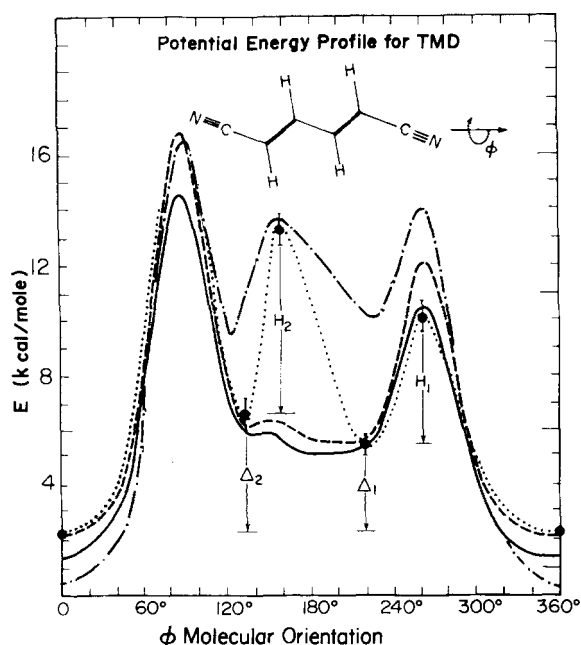


FIG. 11. Intermolecular potential energy in solid TMD as a function of the orientation of a molecule around its long axis. The solid line is the profile calculated in Ref. 10 using atom-atom "6-exp" potential parameters from Refs. 17 and 19, the dashed curve is based on parameters from Refs. 17 and 18, and the dash-dotted line is based on parameters from Refs. 18 and 20. The dotted curve between experimental points represents schematically the energy profile obtained from our NMR data and is similar to the curve in Fig. 9. It should be noted, however, that no independent measurements were made which determined the horizontal positions of these points; the suggested positions indicated in this figure give maximum consistency with theory.

closer in magnitude to H . (Actually, the model used here predicts the disappearance of a relaxation minimum when $\Delta > H$! Thus, the existence of a minimum in our T_1 and T_{1D} results means that, for both mechanisms, $\Delta < H$.) Since $(T_1)_{\min}$ (24 MHz) is only 15 sec, it is possible that the mechanism which dominates T_1 at lower temperatures ($< 200^\circ\text{K}$) also dominates T_{1D} and thus prevents us from observing a similarly long $(T_{1D})_{\min}$ or, at best, leaves a very shallow, almost unobservable minimum (Fig. 5).

Finally, Δ_2 can also be estimated from the experimental $(T_{1D})_{\min}/T_2$ ratio using Eq. (12). Thus, a rough estimate of $\Delta_2 \approx 5 \pm 1$ kcal/mole is obtained, in approximate agreement with values for Δ_2 obtained by the other procedures. Both Δ_1 and Δ_2 should be used to estimate the expected high-temperature (i.e., $\tau_1, \tau_2 \ll T_2$) effects of the molecular reorientations on the protons' second moment. At 20°C , however, only motions involving Δ_1 are effective. We calculated, for motions between the unequal wells of TMD, reductions in the second moment of about 0.5% at 20°C and 2.5% at 150°C , which are small compared to the 6% predicted reduction due to lattice vibrations at room temperature.¹² The larger reduction at 150°C is due to the increased populations of both metastable states at the higher temperature. The fact that these effects on T_2

should be even smaller explains the reason that no such motional narrowing was detected. Nevertheless, it is possible that careful measurements of the second moment as a function of temperature up to the melting point may reveal the combined effect of lattice vibrations and molecular reorientations between TMD's unequal potential wells.

B. Comparison of NMR results with potential energy calculations

In Fig. 11 we present potential energy profiles calculated¹⁰ using different possible van der Waals parameters¹⁷⁻²⁰ for the 6-exp potential function along with our experimentally measured values for Δ_1 , Δ_2 , H_1 , and H_2 . Our measurements resulted in absolute determinations of these quantities *without* adjustable parameters; only the reference energy at 0° orientation was made to fit the profile obtained with parameters from Refs. 17 and 19. The NMR results appear to be somewhat intermediate between the three calculated profiles, demonstrating that none of the sets of van der Waals parameters is completely suitable for TMD reorientations. The calculations indicate that the barriers at 90° and 270° are due primarily to $\text{C} \cdots \text{H}$ interactions, whereas the central barrier is more sensitive to $\text{N} \cdots \text{H}$ interactions. Since there is greater uncertainty in the literature^{15,17,20} regarding $\text{N} \cdots \text{H}$ van der Waals parameters, it is not surprising that the calculations do not show agreement in this central region. Furthermore, the 6-exp potential function may be a poor approximation here since the nitrogen and hydrogen atoms on neighboring molecules may overlap appreciably for these intermediate orientations. As can be seen, the experimental energy differences between the low-lying equilibrium and the metastable states agree well with the corresponding results of potential energy calculations using van der Waals parameters from Refs. 17-19. In view of the approximations involved in such semiempirical calculations, we view the general agreement to be quite satisfactory.

It is interesting to note that our experiments enable us to rule out for TMD a profile calculated¹⁰ using nitrogen parameters of Kuan *et al.*,¹⁵ since it predicts well-differences of 12-13 kcal/mole, which are much higher than our experimental values of 3-4 kcal/mole. Furthermore, with such high energy subminima as those calculated with these parameters, no NMR effects would have been observed due to motions between the wells, since the low-temperature mechanism would then have dominated the relaxation up to the melting point. It seems that the $\text{N} \cdots \text{N}$ parameters, no NMR effects unrealistically high repulsive interactions between hydrogen and nitrogen atoms in TMD. The failure of the use of these parameters in TMD may be due to the fact that they were obtained from data of only one crystal, $\alpha\text{-N}_2$, whereas the carbon and hydrogen parameters of Refs. 18 and 19 were evaluated from data of many hydrocarbons.

C. Other features of NMR relaxation in TMD

There are in the relaxation pattern a few features which are not necessarily associated directly with mo-

tion between inequivalent sites. These are the low-temperature relaxation ($T < 200^\circ\text{K}$), the small drop in T_1 at $312\text{--}314^\circ\text{K}$, and the sharp decrease in T_{1D} from about 385°K up to the melting point. The relaxation pattern observed in the low temperature region suggests that the nuclear spins are probably relaxed via electron paramagnetic impurities. As can be seen in Fig. 7, the magnetization's spin lattice decay in zero field is nonexponential at these temperatures, with a fast initial decay of a small fraction of the dipolar order followed by a slower decay of the residual larger magnetization. Similar T_{1D} effects were observed in CaF_2 doped with paramagnetic impurities.²¹ Support for our assumption that the dominant mechanism for proton relaxation in this temperature region is due to paramagnetic electrons comes from the apparent dependence of T_{1D} at low temperatures on the sample used and on whether it was exposed to elevated temperatures (see Fig. 5). Excessive heating caused sample deterioration which was observed through the appearance of a yellow color in the normally white material. If we assume that the paramagnetic species which causes nuclear relaxation in TMD is free radicals and further assume that the observed deterioration is due to polymerization, we can explain the observed increase in low temperature relaxation times for samples which had been heated. Since polymerization involves a reduction in the free radicals' concentration, such a deterioration of the material will cause an increase in the relaxation times. We detected such a trend at liquid N_2 temperature, for example, where T_{1D} was observed to increase from 24 ± 4 to 66 ± 10 sec after exposure to temperatures of about 150°C . The extremely long relaxation times observed at the lower temperatures indicate that the concentration of paramagnetic impurities (e.g., free radicals) in our solid TMD sample is rather low.

Figure 6 exhibits a sudden drop in T_1 at $312\text{--}314^\circ\text{K}$ at both 24 and 58 MHz. The fact that the temperature of the T_1 discontinuity appears to be independent of frequency suggests that the behavior may be due to a phase transition. However, we are not aware of any x-ray or heat-capacity data at the relevant temperatures which could verify this possibility. At any rate in both the 24 and 58 MHz data the observed effect is rather small (less than 20%) and is not reflected at all in the T_{1D} minimum. Also, the slopes of T_1 (58 MHz) vs $1/T$ before and after the "break" seem to be identical. These results indicate that the previously discussed motions of TMD molecules probably do not participate to any appreciable extent in the possible occurrence of a phase transition in this crystal. Moreover, the invariance of the slopes require that the two structures would probably have to be characterized by very similar well depths and energy barriers for reorientation. From the T_1 (24 MHz) data below the minimum and the experimental Δ_1 we could estimate correlation times for reorientation from the 230° well (see Fig. 12). τ_0 for the room temperature structure was evaluated to be $(2.6 \pm 0.5) \times 10^{-12}$ sec by extrapolation of the corresponding τ 's and is similar to the value $(1.6 \pm 0.5) \times 10^{-12}$ sec obtained for the high temperature structure from the position of the T_1 minimum, assuming the same activation

energy. The τ_0 value evaluated for the 120° well from the $(T_{1D})_{\text{min}}$ position is longer, $(6 \pm 3) \times 10^{-11}$ sec.

The sharp decrease in T_{1D} starting at about 385°K up to the melting point (432°K) is characterized by a slope of 26 ± 3 kcal/mole. Similar large activation energies are associated typically with translational diffusion of entire molecules in the crystal.^{22,23} In many systems diffusional activation energies and lattice sublimation energies are found²² to be typically in the ratio of about 2.0–2.5. A comparison of our measured high-temperature activation energy (26 ± 3 kcal/mole) with the calculated¹⁰ lattice energy (9–10 kcal/mole) gives a similar ratio for TMD, thus supporting the idea that the high temperature mechanism is translational diffusion of the TMD molecule. Such motions usually average out large portions of the dipolar local fields and result in T_{1D} minimum values of the order of T_2 . Due to the crystal's melting temperature being at 159°C , the minimum in T_{1D} corresponding to the above process could not be observed. At any rate the relatively short T_{1D} values observed prior to the melting of TMD suggest a strong-collision diffusion process between equal potential wells.

VI. CONCLUSIONS

This paper demonstrates that NMR relaxation may provide a powerful tool for studying asymmetric potential surfaces in solids. By modifying and applying the basic NMR theory^{4,5} to each particular system, it is possible to evaluate from the relaxation data such quantities as energy barriers for molecular reorientations and relative depths of potential wells. It should be noted that, although motions between unequal wells lead to a unique and distinct relaxation pattern, they do not constitute a very efficient relaxation mechanism, especially when the wells differ considerably in depth so that only a very small fraction of the dipolar field is modulated. Consequently, this mechanism will often be masked by other mechanisms such as motions between equal wells or paramagnetic relaxation. Therefore, in order to study orientational defects by NMR, it is generally desirable to have very pure crystals composed of molecules which do not have easily rotating symmetric groups.

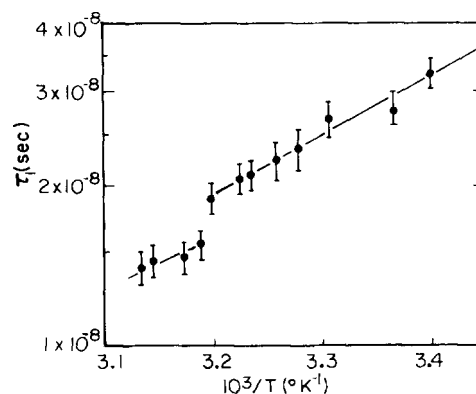


FIG. 12. Correlation times τ_1 vs inverse temperature for reorientations from the 230° well. The values for τ_1 were obtained from the T_1 (24 MHz) data using Eq. (14a).

Calculations of potential energy surfaces, such as were done for TMD,¹⁰ are desirable either in predicting possible motions in solids or in identifying the actual mechanism of experimentally detected motion. However, it should be realized that such semiempirical calculations in their present state of art can yield only qualitative information, especially when close contacts and strong repulsion between atoms are involved. Nevertheless, as we have demonstrated for TMD, the combination of NMR relaxation measurements of re-orienting molecules and complementary potential energy calculations can detect orientational defects in crystals and lead to a better understanding of their detailed structure. Furthermore, as we have shown, such studies may allow different models for interatomic forces to be distinguished in a particular molecular crystal.

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